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In re Application of:
Plantenga, F. et al.

Serial No: 09/540,400

Filing Date: March 31, 2000

For: PROCESS FOR EFFECTING ULTRA-DEEP
HDS OF HYDROCARBON FEEDSTOCKS



Docket No: ACH 2696

Examiner: Walter Dean Griffin

Group Art Unit: 1764

Commissioner for Patents
P.O. Box 1450
Alexandria, VA 22313-1450

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Respectfully submitted,

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IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

In re Application of:

Frans L. Plantenga, et al

Serial No.: 09/540,400

Filing Date: March 31, 2000

For: PROCESS FOR EFFECTING ULTRA DEEP:
HDS OF HYDROCARBON FEEDSTOCKS :



: Docket: ACH 2696US

: Examiner: Walter Dean Griffin

: Group Art Unit: 1764

SUBMISSION OF CERTIFIED COPY OF PRIORITY DOCUMENT

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P.O. Box 1450
Alexandria, VA 22313-1450

Sir:

Enclosed herewith is a certified copy of European Patent Application No.

99201016.5, filed on April 2, 1999.

Respectfully submitted,

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Attestation

Die angehefteten Unterlagen stimmen mit der ursprünglich eingereichten Fassung der auf dem nächsten Blatt bezeichneten europäischen Patentanmeldung überein.

The attached documents are exact copies of the European patent application described on the following page, as originally filed.

Les documents fixés à cette attestation sont conformes à la version initialement déposée de la demande de brevet européen spécifiée à la page suivante.

Patentanmeldung Nr. Patent application No. Demande de brevet n°

99201016.5

Der Präsident des Europäischen Patentamts:
Im Auftrag

For the President of the European Patent Office

Le Président de l'Office européen des brevets
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**Blatt 2 der Bescheinigung
Sheet 2 of the certificate
Page 2 de l'attestation**

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Anmelder:
Applicant(s):
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Titre de l'invention:

Process for effecting deep hydrodesulphurisation of hydrocarbon feedstocks

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See for original title of the application page 1 of the description.

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PROCESS FOR EFFECTING DEEP HDS OF HYDROCARBON FEEDSTOCKS

5 The present invention relates to a process for effecting deep HDS of hydrocarbon feedstocks.

10 In an effort to regulate SO₂ emissions from the burning of fuels, the environmental regulations as to the sulphur content of fuels, in particular diesel fuels, are becoming more and more strict. In Europe diesel feedstocks will be required as of 2000 to have a sulphur content below 350 ppm, while as of 2005, the sulphur content should be below 50 ppm, with even further decreases not being excluded. In consequence, there is an increasing need for catalyst systems which
15 point of 450°C or less to below 200 ppm, preferably below 100 ppm, even more preferably below 50 ppm, calculated by weight as elemental sulphur on the total liquid product.

20 In the context of the present specification the term deep HDS means the reduction of the sulphur content of a hydrocarbon feedstock to a value of less than 200 ppm, preferably less than 100 ppm, and even more preferably to a value of less than 50 ppm, calculated by weight as elemental sulphur on the total liquid product, as determined in accordance with ASTM D-4294. The indications Group VIB and Group VIII correspond to the Periodic Table of Elements applied by
25 Chemical Abstract Services (CAS system).

We have now found that a very efficient process for reducing the sulphur content of a hydrocarbon feedstock to a value of less than 200 ppm can be obtained if a catalyst is applied therein which before sulphidation comprises a Group VIB metal
30 component, a Group VIII metal component, and an organic additive.

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The catalyst

Catalysts which before sulphidation comprise a Group VIB metal component, a Group VIII metal component, and an organic additive are known in themselves in the art.

For example, European patent application 0 601 722 describes a process for preparing a catalyst in which a gamma-alumina support is impregnated with an impregnation solution comprising a Group VIB metal component, a Group VIII metal component, and an organic additive which is at least one compound selected from the group of compounds comprising at least two hydroxyl groups and 2-10 carbon atoms, and the (poly)ethers of these compounds.

WO 96/41848 describes a process in which an additive-containing catalyst is prepared by incorporating the additive mentioned above into a finished catalyst composition. That is, a catalyst composition comprising hydrogenation metal components in the oxidic form, brought into that form by calcination, is contacted with the specified additive.

European patent application 98203305 describes a process for preparing an additive-containing catalyst wherein the catalyst composition is subjected to an ageing step after incorporation of the additive.

Japanese patent application 04-166231 describes a process for preparing a hydrotreating catalyst in which a support is impregnated with an impregnation solution comprising a Group VIB metal component, a Group VIII metal component, and, optionally, a phosphorus component. The support is dried at a temperature below 200°C, contacted with a polyol, and then dried again at a temperature below 200°C.

Japanese patent application 04-166233 describes substantially the same process as the above-mentioned patent application, except that instead of a polyol an alkoxycarboxylic acid is used.

Japanese patent application 06-339635 describes a process in which a support is impregnated with an impregnation solution comprising an organic acid, Group VIB and Group VIII hydrogenation metal components, and preferably a phosphorus component. The impregnated support is dried at a temperature

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below 200°C. The dried impregnated support is contacted with an organic acid or polyol, after which the thus treated support is dried at a temperature below 200°C. Japanese patent application 06-210182 describes a process for preparing a catalyst in which a boria-alumina support comprising 3-15 wt.% of boria is
5 impregnated with an Impregnation solution comprising a Group VIB metal component, a Group VIII metal component, and a polyol. The impregnated support is dried at a temperature of 110°C to form a catalyst.

In principle, any catalyst prepared by any process according to any one of the
10 above references or not which comprises a Group VIB hydrogenation metal, a Group VIII hydrogenation metal, and an organic additive on a carrier is suitable for use in the process of the present invention. As Group VIB metals may be mentioned molybdenum, tungsten, and chromium. Group VIII metals include nickel, cobalt, and iron. In the deep HDS process of the present invention, it is
15 preferred to use a catalyst comprising molybdenum as Group VIB metal component and nickel and/or cobalt as Group VIII metal component. The use of nickel as Group VIII metal component is particularly preferred.

The catalyst usually has a metal content in the range of 0.1 to 50 wt.%, calculated on the dry weight of the catalyst not containing the additive. The Group VIB metal
20 will frequently be present in an amount of 5-30 wt.%, preferably 15-25 wt.%, calculated as trioxide. The Group VIII metal will frequently be present in an amount of 1-10 wt.%, preferably 2-6 wt.%, respectively, calculated as monoxide. If so desired, the catalyst may also contain other components, such as phosphorus, halogens, and boron. Particularly, the presence of phosphorus in an
25 amount of 1-10 wt.%, calculated as P_2O_5 , can be preferred.

The catalyst carrier may comprise the conventional oxides, e.g., alumina, silica, silica-alumina, alumina with silica-alumina dispersed therein, silica-coated alumina, magnesia, zirconia, boria, and titania, as well as mixtures of these oxides. As a rule, preference is given to the carrier comprising alumina, silica-
30 alumina, alumina with silica-alumina dispersed therein, or silica-coated alumina. Special preference is given to the carrier consisting essentially of alumina or alumina containing up to 10 wt.% of silica. A carrier containing a transition

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alumina, for example an eta, theta, or gamma alumina is preferred within this group, with a gamma-alumina carrier being especially preferred.

The catalyst's pore volume (measured via mercury penetration) is not critical to the process according to the invention and will generally be in the range of 0.25 to

5 1 ml/g. The specific surface area is not critical to the process according to the invention either and will generally be in the range of 50 to 400 m²/g (measured using the BET method). Preferably, the catalyst will have a median pore diameter in the range of 7-15 nm, as determined by mercury porosimetry (contact angle 130°), and at least 60% of the total pore volume will be in the range of ± 2 nm
10 from the median pore diameter.

The catalyst is suitably in the form of spheres or extrudates. Examples of suitable types of extrudates have been disclosed in the literature (see, int. al., US 4 028 227). Highly suitable for use are cylindrical particles (which may be hollow or not) as well as symmetrical and asymmetrical polylobed particles (2, 3 or 4 lobes).

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The organic additive present in the catalyst to be used in the process according to the invention before sulphidation may be any organic additive. Preferably the organic additive is selected from the group of compounds comprising at least two oxygen atoms and 2 - 10 carbon atoms and the compounds built up from these
20 compounds. Organic compounds selected from the group of compounds comprising at least two oxygen-containing moieties, such as a carboxyl, carbonyl or hydroxyl moieties, and 2 - 10 carbon atoms and the compounds built up from these compounds are preferred. Examples of suitable compounds include citric acid, tartaric acid, oxalic acid, malonic acid, malic acid, butanediol, pyruvic
25 aldehyde, glycolic aldehyde, and acetaldol. At this point in time, preference is given to an additive that is selected from the group of compounds comprising at least two hydroxyl groups and 2-10 carbon atoms per molecule, and the (poly)ethers of these compounds. Suitable compounds from this group include aliphatic alcohols such as ethylene glycol, propylene glycol, glycerin, trimethylol
30 ethane, trimethylol propane, etc. Ethers of these compounds include diethylene glycol, dipropylene glycol, trimethylene glycol, triethylene glycol, tributylene glycol, tetraethylene glycol, tetrapentylene glycol. This range can be extrapolated to include polyethers like polyethylene glycol. For this last compound,

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with the carrier material before it is shaped, or by impregnating the shaped carrier material with the additive.

It is also possible to incorporate the additive into the catalyst composition simultaneously with the hydrogenation metal components. This can be done, e.g.,

5 by mixing the additive and the hydrogenation metal components with the carrier material before shaping. However, a preferred way to incorporate the additive into the catalyst composition simultaneously with the hydrogenation metal components is by impregnating the carrier with an impregnation solution comprising the hydrogenation metal components and the additive, followed by
10 drying under such conditions that at least part of the additive is maintained in the catalyst. This is the process described in EP 601 722.

It is also possible to incorporate the additive into the catalyst composition subsequent to the hydrogenation metal components. This can be done, e.g., by first incorporating the hydrogenation metal components into the catalyst
15 composition, e.g., by mixing them with the carrier material or by impregnating the carrier with them, optionally followed by drying, and subsequently incorporating the additive, e.g., by impregnation. A preferred embodiment of this process is the embodiment described in WO 96/41848, in which first a catalyst composition is prepared by incorporating hydrogenation metal components into a catalyst
20 composition, e.g., by impregnation of a carrier, after which the catalyst is subjected to a calcination step to convert the hydrogenation metal components into their oxides, followed by incorporating the additive into the catalyst composition by impregnation. In this embodiment it is possible, e.g., to composite a conventional hydrotreating catalyst comprising a hydrogenation metal
25 component on a carrier with the additive. The conventional hydrotreating catalyst used in this process can be either a freshly prepared hydrotreating catalyst or a used hydrotreating catalyst which has been regenerated.

At present the catalysts prepared by the processes described in EP 0601 722 and WO 96/41848 are considered preferred.

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The sulphidation step

The first step of the process according to the invention is to subject the additive-containing hydrotreating catalyst to a sulphiding step. In the context of the present specification, the indication sulphiding step or sulphidation step is meant to include any process step in which at least a portion of the hydrogenation metal components present in the catalyst is converted into the sulphidic form, either directly or after an activation treatment with hydrogen.

Suitable sulphidation processes are known in the art. *Ex situ* sulphidation processes take place outside the reactor in which the catalyst is to be used in hydrotreating hydrocarbon feeds. In such a process the catalyst is contacted with a sulphur compound, e.g. a polysulphide or elemental sulphur, outside the reactor and, if necessary, dried. In a second step, the material is treated with hydrogen gas at elevated temperature in the reactor, optionally in the presence of a feed, to activate the catalyst, i.e. bring it into the sulphided state.

In situ sulphidation processes take place in the reactor in which the catalyst is to be used in hydrotreating hydrocarbon feeds. Here, the catalyst is contacted in the reactor at elevated temperature with a hydrogen gas stream mixed with a sulphiding agent, such as hydrogen sulphide or a compound which under the prevailing conditions is decomposable into hydrogen sulphide. It is also possible to use a hydrogen gas stream combined with a hydrocarbon feed comprising a sulphur compound which under the prevailing conditions is decomposable into hydrogen sulphide. In the latter case it is possible to use a hydrocarbon feed comprising an added sulphiding agent (a so-called spiked feed), but it is also possible to use a sulphur-containing hydrocarbon feed without any added sulphiding agent, since the sulphur components present in the feed will be converted into hydrogen sulphide in the presence of the catalyst. The hydrocarbon feed may be the feed to be subjected to deep HDS in the process according to the invention, but it may also be a different feed, later to be replaced with the feed to be subjected to deep HDS. Combinations of the various sulphiding techniques may also be applied.

In the context of the present invention it is preferred to sulphide the catalyst by contacting it with an, optionally spiked, hydrocarbon feed.

The feed

The feedstock suitable for use in the process according to the invention has a
5 95% boiling point, as determined in accordance with ASTM D-1160, of 450°C or
less, preferably 420°C or less, more preferably 400°C or less. That is, 95 vol.% of
the feedstock boils at a temperature of 450°C or less, preferably 420°C or less,
more preferably 400°C or less. Generally, the initial boiling point of the feedstock
is above 100°C, preferably above 180°C. The feed contains less than 500 ppm of
10 sulphur, preferably 150-500 ppm of sulphur.

The feedstock to be used in the process according to the invention may be
prepared by hydrodesulphurisation of starting hydrocarbon feedstocks containing
0.1 wt.% or more of sulphur, preferably 0.2 to 2.5 wt.% of sulphur, more
15 preferably 0.5 to 2.0 wt.% of sulphur. This starting feedstock generally has a 95%
boiling point, as determined in accordance with ASTM D-1160, of 450°C or less,
preferably 420°C or less, more preferably 400°C or less. Generally, the initial
boiling point of the feedstock is above 100°C, preferably above 180°C. The
feedstock generally contains 20-1200 ppm nitrogen, preferably 30-800 ppm, more
20 preferably 70-600 ppm. The metal content of the feedstock preferably is less than
5 ppm, more preferably less than 1 ppm (Ni+V). Examples of suitable starting
feedstocks are feedstocks comprising one or more of straight run gas oil, light
catalytically cracked gas oil, and light thermally cracked gas oil.

The above-mentioned starting hydrocarbon feedstock is subjected to
25 hydrodesulphurisation to reduce its sulphur content to a value below 500 ppm.
This hydrodesulphurisation process can be carried out using conventional
hydrodesulphurisation catalysts comprising a Group VIB metal component, a
Group VIII metal component, and, optionally, phosphorus on a carrier comprising
alumina. Suitable hydrodesulphurisation catalysts are commercially available,
30 and include for example KF 756 and KF 901 of Akzo Nobel. It is also possible to
obtain the feedstock for the process according to the invention from a starting
feedstock containing more sulphur by means of a two-step process, such as
those described in EP 0 464 931, EP-A 0 523 679 or EP 870 807.

Additionally, It is also possible to obtain the feedstock for the process of the invention from the above-mentioned starting feedstock by using an additive-based catalyst. The present invention thus also relates to a two-step process for
5 converting a starting feedstock having a sulphur content of above 0.1 wt.% into a product having a sulphur content of 200 ppm or less, wherein the process comprises sulphidation of a first and a second catalyst comprising a Group VIB metal component, a Group VIII metal component, and an organic additive on a carrier, contacting a feedstock with a 95% boiling point of 450°C or less and a
10 sulphur content of 0.1 wt.% or more with the first sulphided catalyst under conditions of elevated temperature and pressure to form a product with a sulphur content of less than 500 ppm, and contacting the effluent from the first catalyst, optionally after fractionation or intermediate phase separation, optionally including removal of H₂S and NH₃ formed, with the second sulphided catalyst under
15 conditions of elevated temperature and pressure to form a product with a sulphur content of less than 200 ppm.

In this process, the first and second catalysts containing an organic additive before sulphidation may be the same or different. It is considered preferred at this point in time for the first catalyst to comprise molybdenum as Group VIB metal
20 component and cobalt and/or nickel as Group VIII metal component, with the second catalyst comprising molybdenum as Group VIB metal component and nickel as Group VIII metal component. The two-step process can be carried out in one or two reactors, as may be desired.

25 The process conditions

The process according to the invention is carried out at elevated temperature and pressure. The temperature generally is 200-450°C, preferably 280-430°C. The reactor inlet hydrogen partial pressure generally is 5-200 bar, preferably 10-100
30 bar, more preferably 15-50 bar. The liquid hourly space velocity preferably is between 0.1 and 10 vol./vol.h, more preferably between 0.5 and 4 vol./vol.h. The H₂/oil ratio generally is in the range of 50-2000 Nl/l, preferably in the range of 80-500 Nl/l.

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The process conditions are selected in such a way that the sulphur content of the total liquid effluent is less than 200 ppm, preferably less than 100 ppm, more preferably less than 50 ppm. The exact process conditions will depend, int. al., on the nature of the feedstock, the desired degree of hydrodesulphurisation, and the nature of the catalyst. In general, a higher temperature, a higher hydrogen partial pressure, and a lower space velocity will decrease the sulphur content of the final product. The selection of the appropriate process conditions to obtain the desired sulphur content in the product is well within the scope of the person skilled in the art of hydroprocessing.

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Example 1: Nickel-molybdenum catalysts in deep-HDSPreparation of additive-containing catalyst

Extrudates of a gamma-alumina carrier were impregnated to pore volume saturation with an impregnation solution comprising a molybdenum compound, a nickel compound, phosphoric acid, and diethylene glycol, after which the impregnated carrier was dried at a temperature of 100°C for a period of 16 hours. The final catalyst contained 20 wt.% of molybdenum, calculated as trioxide, 5 wt.% of nickel, calculated as oxide, and 5 wt.% of phosphorus, calculated as P_2O_5 . All weight percentages are calculated on the dry catalyst base, not including the additive. The molar ratio between DEG and the total of Ni and Mo is 0.4.

Preparation of comparative catalyst

A catalyst was prepared in the manner described above, except that the impregnation was carried out in the absence of DEG, and that the impregnated catalyst was subjected to a calcination step at 500°C for 2 hours.

The catalyst had the same composition as that described above, except for the absence of DEG.

30

The two catalysts were tested side by side in an upflow tubular reactor. Each reactor tube contained 75 ml of catalyst homogeneously intermixed with 80 ml of carborundum particles.

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The catalysts were sulphided using an SRLGO in which dimethyl disulphide had been dissolved to a total S content of 2.5 wt.%.
 The feed applied was a diesel feedstock with the following properties.

Nitrogen (ASTM D-4629) (ppmwt)	28
Sulphur (ASTM D-4294) (wt.%)	219
Density 15°C (g/ml)	0.8490
Dist. (°C)	D86*
IBP	213
5 vol.%	234
10 vol.%	242
30 vol.%	266
50 vol.%	286
70 vol.%	308
90 vol.%	334
95 vol.%	347
FBP	360

* The boiling range of the feedstock is determined according to ASTM D-86 can be converted to a boiling range in accordance with ASTM D-1160 by calculation. The 95% boiling point of the above-mentioned feedstock in accordance with ASTM D-1160 is below 450°C.

The catalysts were tested under four test conditions. The first three test conditions differ in terms of the pressure applied. The fourth test condition differs from the first test condition in that the feed was spiked with 1 wt.% of dimethyl disulphide and 100 ppm t-butyl amine. This was done to simulate the conditions halfway down a commercial unit, where the feed contacting the catalyst contains ammonia and hydrogen sulphide generated in the first part of the unit.

The conditions and test results are given in the following tables.

Reaction conditions

	condition 1	condition 2	condition 3	condition 4
feed	F1	F1	F1	F1 + S + N
Temperature (°C)	323	323	323	323
Pressure (bar)	30	60	15	30
H ₂ /oil (NI/I)	300	300	300	300
LHSV (h-1)	2	2	2	2

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Sulphur analysis of products obtained

	Catalyst according to the invention	Comparative Catalyst
condition 1 (30 bar)	13 ppm S	30 ppm S
condition 2 (60 bar)	< 5 ppm S	7 ppm S
condition 3 (15 bar)	16 ppm S	47 ppm S
condition 4 (30 bar, spiked feed)	36 ppm S	not determined

The above shows that particularly at low pressures the use of a catalyst which before sulphidation contains an organic additive gives a much improved sulphur removal as compared with the use of a conventional additive-free catalyst.

Example 2: Cobalt-molybdenum catalysts in deep-HDSPreparation of additive-containing catalyst

10 Extrudates of a gamma-alumina carrier were impregnated to pore volume saturation with an impregnation solution comprising a molybdenum compound, a cobalt compound, phosphoric acid, and polyethylene glycol, after which the impregnated carrier was dried at a temperature of 100°C for a period of 16 hours. The final catalyst contained 20 wt.% of molybdenum, calculated as trioxide, 5
15 wt.% of cobalt, calculated as oxide, and 3 wt.% of phosphorus, calculated as P_2O_5 . All weight percentages are calculated on the dry catalyst base, not including the additive. The molar ratio between PEG and the total of Co and Mo is 0.4.

Preparation of comparative catalyst

20 A catalyst was prepared in the manner described above, except that the impregnation was carried out in the absence of PEG and the impregnated catalyst was subjected to a calcination step at 500°C for 2 hours. The catalyst had the same composition as that described above, except for the
25 absence of PEG.

The two catalysts were subjected to the test procedure described in Example 1. The results are given in the following table.

Sulphur analysis of products obtained

	Catalyst according to the invention	Comparative Catalyst
condition 1 (30 bar)	30 ppm S	54 ppm S
condition 2 (60 bar)	11 ppm S	31 ppm S
condition 3 (15 bar)	32 ppm S	59 ppm S
condition 4 (30 bar, spiked feed)	52 ppm S	83 ppm S

5 It is clear from the above that the use of a catalyst which before sulphidation contains an additive shows an improved deep-HDS activity under all conditions as compared with a conventional additive-free catalyst.

A comparison with the results of Example 1 shows that the nickel-containing catalyst of Example 1 shows better results in deep-HDS than the cobalt-containing catalyst of the present example.

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CLAIMS

1. A process for reducing the sulphur content of a hydrocarbon feedstock to
5 a value of less than 200 ppm, comprising subjecting a catalyst comprising
a Group VIB metal component, a Group VIII metal component, and an
organic additive on a carrier to a sulphidation step, and contacting a
feedstock with a 95% boiling point of 450°C or less and a sulphur content
10 of 500 ppm or less with the sulphided catalyst under conditions of
elevated temperature and pressure to form a product with a sulphur
content of less than 200 ppm.
2. The process of claim 1 wherein the organic additive is at least one
15 compound selected from the group of compounds comprising at least two
hydroxyl groups and 2-10 carbon atoms, and the (poly)ethers of these
compounds.
3. The process of claim 2 wherein the additive is at least one compound
20 selected from ethylene glycol, diethylene glycol, triethylene glycol,
tetraethylene glycol, propylene glycol, dipropylene glycol and
polyethylene glycol with a molecular weight between 200 and 600.
4. The process of claim 2 wherein the additive is a saccharide or a
25 polysaccharide.
5. The process of any one of the preceding claims wherein the sulphidation
step is carried out *in situ*, optionally using the feed which is to be
subjected to deep-HDS with the sulphided catalyst.
- 30 6. A two-step process for converting a starting feedstock having a sulphur
content of above 0.1 wt.% into a product having a sulphur content of 200
ppm or less, wherein the process comprises sulphidation of a first and a
second catalyst comprising a Group VIB metal component, a Group VIII

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metal component, and an organic additive on a carrier, contacting a feedstock with a 95% boiling point of 450°C or less and a sulphur content of 0.1 wt.% or more with the first sulphided catalyst under conditions of elevated temperature and pressure to form a product with a sulphur content of less than 500 ppm, and contacting the effluent from the first catalyst, optionally after fractionation or intermediate phase separation, with the second sulphided catalyst under conditions of elevated temperature and pressure to form a product with a sulphur content of less than 200 ppm.

7. The process of claim 6 wherein the first catalyst comprises molybdenum as Group VIB metal component and cobalt and/or nickel as Group VIII metal component, while the second catalyst comprises molybdenum as Group VIB metal component and nickel as Group VIII metal component.

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ABSTRACT

The invention pertains to a process for reducing the sulphur content of a hydrocarbon feedstock to a value of less than 200 ppm which comprises
5 subjecting a catalyst comprising a Group VIB metal component, a Group VIII metal component, and an organic additive on a carrier to a sulphidation step, and contacting a feedstock with a 95% boiling point of 450°C or less and a sulphur content of 500 ppm or less with the sulphided catalyst under conditions of
10 elevated temperature and pressure to form a product with a sulphur content of less than 200 ppm.

The organic additive preferably is at least one compound selected from the group of compounds comprising at least two hydroxyl groups and 2-10 carbon atoms, and the (poly)ethers of these compounds.